CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE (PVDF) HOLLOW FIBER MEMBRANE ON DIFFERENT LITHIUM CHLORIDE (LiCl) LOADING FOR CARBON DIOXIDE (CO_2) REMOVAL

NOR ATIKAH BINTI MOHD

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ABSTRACT

In this study, hollow fiber membranes (PVDF – LiCl) were studied as one of the efficient alternatives for carbon dioxide removal. The membranes were prepared via phase inversion method by using the wet spinning process. An aqueous dimethylacetamide (DMAc) solution was used as a solvent. The experimental was conducted to investigate the effect of different lithium chloride (LiCl) concentration on the membrane properties and membrane structure. The prepared fibers were characterized in term of gas permeation, critical water entry pressure (CEPw), water contact angle and morphology analysis. Results of gas permeation test showed that with increasing of LiCl concentration, the pore size of membrane became smaller and increased in the effective surface porosity. The cross-section, inner surface and outer surface of membranes were examined via scanning electron microscopy (SEM). It gave a result that by addition of LiCl, membrane structure change from finger-like to sponge-like layer, which resulted in a high wetting pressure and N_2 permeation rates. Membrane with 5% LiCl gave higher hydrophobicity than plain PVDF and 3% LiCl membrane. It was suggested that higher hydrophobicity of PVDF membrane may be an effective way for long-term operating performance of CO_2 removal. Therefore, these results concluded that small pore size, high surface porosity and high wetting resistance are the important factors in producing an efficient membrane for CO_2 removal.

ABSTRAK

Dalam kajian ini, membran gentian geronggang (PVDF - LiCl) telah dikaji sebagai salah satu alternatif berkesan untuk penyerapan karbon dioksida. Membran disediakan melalui kaedah fasa penyongsangan dengan menggunakan proses berputar pelarut. Larutan dimethylacetamida (DMAc) telah digunakan sebagai pelarut. Eksperimen ini dijalankan untuk mengkaji kesan kepekatan litium klorida (LiCl) yang berbeza terhadap sifat membran dan struktur membran. Gentian yang tersedia telah dicirikan dari segi penyerapan gas, tekanan kemasukan air kritikal (CEPw), sudut sentuhan air dan analisis morfologi. Keputusan ujian penyerapan gas menunjukkan bahawa dengan peningkatan kepekatan LiCl, saiz liang membran menjadi lebih kecil dan peningkatan keliangan permukaan berkesan. Keratan rentas, permukaan dalaman dan permukaan luar membran telah diperiksa melalui mikroskop imbasan elektron (SEM). Ia menunjukkan keputusan apabila ada penambahan LiCl, struktur membran berubah daripada seperti bentuk jejari kepada seperti bentuk lapisan span, yang mengakibatkan tekanan kebasahan dan kadar penyerapan N_2 menjadi tinggi. Membran dengan 5% LiCl memberi *hydrophobicity* yang lebih tinggi daripada PVDF biasa dan membran 3% LiCl. Ia telah dicadangkan bahawa membran PVDF yang mempunyai *hydrophobicity* tinggi boleh menjadi cara yang berkesan untuk prestasi operasi jangka panjang bagi penyingkiran CO_2. Oleh itu, kesimpulannya bahawa saiz liang kecil, keliangan permukaan yang tinggi dan rintangan kebasahan tinggi adalah faktor penting dalam menghasilkan membran berkesan untuk penyingkiran CO_2.

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cm	centi meter
K_o	slope
nm	nano meter
ppm	part per million
P_o	intercept
µm	micro meter
^oC	degrees Celcius

LIST OF ABBREVIATIONS

CEPw	Critical water entry pressure
CO_2	Carbon dioxide
EPA	Environmental protection agency
NMP	N-methylpyrrolidone
PE	Polyethylene
PES	Polyethersulfone
PP	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
LiCl	Lithium cloride
N_2	Nitrogen gas

CHAPTER 1

INTRODUCTION

1.1 Background Study

Carbon dioxide (CO_2) is one of the most important greenhouse gases that result from human activities such as industrial and domestic usage. Carbon dioxide (CO_2) emissions have a negative impact on global warming. Therefore, it is very important to remove carbon dioxide (CO_2) from the flue gas stream and the local industry as an effort to deal with issues of climate change in the future (Mansourizadeh and Ismail, 2011). In addition, human concerns regarding the level of carbon dioxide (CO_2) emissions to the atmosphere will affect the economy and demand for gas purification equipment will increase in the future (Rahbari Sisakht et al, 2012).

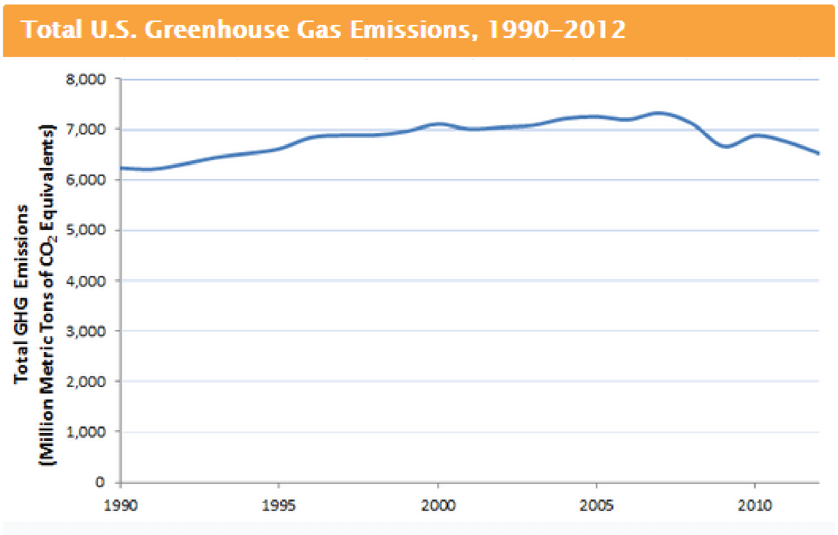

Figure 0-1: Emission estimates from the Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2012

Based on Figure 1-1, line graph showed the total United State (U.S.) greenhouse gas emissions for 1990 to 2012. The total greenhouse gas emissions steadily increased from just over 6,000 million metric tons of carbon dioxide equivalents in 1990 to over 7,000 million around 2000. Between 2007 and 2009, the greenhouse gas emissions decline to about 6,600 million metric tons of carbon dioxide equivalents, followed by a slight rebound in 2010 and 2011 to around 6,800 million metric tons and a slight decline in 2012 to around 6,500 million metric tons. Hence, it can be summarized that carbon dioxide (CO_2) emissions in the United States increased by about 5% between 1990 and 2012.

Releasing of carbon dioxide to atmosphere can bring harm to the environment because the acid contents in carbon dioxide (CO_2) gas are hazardous. According to United State Environment Protection Agency (EPA), in 2012, greenhouse gas emissions totalled 6,526 million metric tons of carbon dioxide (CO_2). This problem caused temperature of the planet increase (global warming). Currently, the amount of carbon dioxide in the atmosphere is increasing at the rate of about one part per million per year (ppm). If this continues, some meteorologists expect that the temperature of the earth will increase by about 2.5 degrees celsius and it could be to cause glaciers to melt, which would cause coastal flooding. The changing climate impacts society and ecosystems, such as climate change can increase or decrease rainfall, influence agricultural growth, affect human health, cause changes to forests, animal habitats and other ecosystems.

Therefore, it is important to lower the negative impact of environment. Priority should be given to the technologies with enhanced carbon dioxide (CO_2) removal efficiency that can minimize the impacts. Membrane technology is one of the promising alternatives for carbon dioxide (CO_2) removal due to its favourable mass transfer performance (Mansourizadeh and Ismail, 2011).

Numerous studies have been conducted for CO_2 removal by using the hollow fiber membrane, e.g. Nishikawa et al. (1995), Klaassen and Jansen (2001), Chen and Li (2005), Rongwong et al. (2009), Mansourizadeh et al. (2010), Khaisri et al. (2011), Mansourizadeh, A. (2012), Naim et al. (2013), and Rezaaei et al. (2015). For carbon dioxide (CO_2) absorption study, some of the microporous hydrophobic membrane was used, which are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). Although the physical and chemical properties of membranes is well understood, the improvement of the membrane structure must be always explored by the researchers to get the most effective membrane structure for efficient CO_2 removal. In this study, polyvinylidene fluoride (PVDF) was used because it is hydrophobic polymers dissolved in the some solvent, which can be used in phase-inversion process for the preparation of asymmetric membranes. This membrane showed in easy controlled membrane structure and morphology (Rezaei et al, 2014).

In recent years, several methods have been carry out for capturing of carbon dioxide (CO_2), such as chemical and physical absorption, solid adsorption, cryogenic distillation, and membrane separation (Naim and Ismail, 2013). Microporous hollow fiber membrane contactor system for carbon dioxide (CO_2) absorption is has attracted researchers' attention to apply this in carbon dioxide (CO_2) absorption because gas and liquid can contact on the gas-liquid interface at the mouth of each membrane pore (Naim et al., 2013). Mansourizadeh, (2012) studied that the membrane was the most important element of the membrane contactor. Effective membrane required high hydrophobicity, high surface porosity, low mass transfer resistance and excellent resistance to get a better result performance.

Li and Chen (2005) reported that Qi and Cussler were the first to establish the idea of the hollow-fiber contactor using a microporous polypropylene (PP) hollow fiber membrane for absorption of carbon dioxide (CO_2) and aqueous sodium hydroxide solution was used as an absorbent.

In this study, a microporous PVDF membrane is one of the promising candidates for use in membrane contactors due to relatively high hydrophobicity, high chemical resistance and reasonable material cost (Rajabzadeh et al, 2009). PVDF is the only hydrophobic polymer that can be dissolved in common solvents to prepare asymmetric membranes via phase-inversion process (Mansourizadeh and Pouranfard, 2014). LiCl was used as an additive in PVDF/ Dimethylacetamide (DMAc) solution systems for the evolution of high performance hollow fiber membranes. The influence of LiCl concentration on the final membrane structure and the resulting of gas permeation, critical water entry pressure (CEPw), and water contact angle were analyzed (Yeow et al, 2005). This work therefore aims to determine the most efficient characteristics of hollow fiber membrane to reduce the carbon dioxide by using absorption method.

1.2 Problem statement

One of the main challenges of membrane gas absorption technology is the pore wetting that occurs during the research. This problem can reduce the mass transfer coefficient of the membrane module. The main cause of pore wetting is capillary condensation (Naim et al., 2013). According to Dindore et al. (2004), they reported that this problem depends on a number of membrane properties such as pore size, hydrophobicity, surface roughness and chemical resistance to solvents, on the surface tension of solvent and operating conditions of absorption process. Therefore, it is possible to lower the wet ability of membranes by reducing the membrane pore size and increasing the surface of membrane (Rongwong et al., 2009).

1.3 Objectives

The following are the objectives of this research:

1) To prepare the PVDF hollow fiber membrane via phase inversion process.
2) To study the effect of lithium chloride (LiCl) loading on the membrane properties and membrane structure.

1.4 Scope of this research

The following are the scope of this research:-

1) The polyvinylidene fluoride (PVDF) polymer dope making by using lithium chloride (LiCl) as an additive and spinning process for obtaining hollow fiber membrane.

2) Characterization of PVDF hollow fiber membrane in term of gas permeation, critical water entry pressure (pr), water contact angle and morphology analysis by using scanning electron microscopy (SEM).

1.5 Organisation of the thesis

Chapter 1 Present the research background of CO_2 removal by membrane gas absorption process, determine the motivation, problem statement, objectivities, scope f the research and structure of this thesis.

Chapter 2 Present the overview of the research. A general definition and type of membrane module were defined. A description of hollow fiber membrane, lithium cloride as an additives and as well as behaviour of membranes that can also be described with additional dimensionless numbers. This chapter also provides a brief review on previous research done on hollow fiber membrane and a method to prepared hollow fiber membranes..

Chapter 3 gives a description of the methodology of this research work including the chemicals and equipment’s used. The methods of membranes fabrication and characterization also was described in details, and observe the changes of membrane surface morphologies by scanning electron microscopy (SEM) in this chapter.

Chapter 4 Investigate the effects of different concentration of lithium chloride (LiCl) on membrane fiber characteristics and morphology.

Chapter 5 Presents about the final conclusion and summarise of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter will point out about the definition and the basic concept of membrane technology, membrane structure that have been used nowadays, membrane module in gas removal industry and also characteristic of membranes involve in this research.

2.2 Introduction to membrane

2.2.1 Membrane definition

Membrane can defined in various terms of definition, basically as thin layer of semi-permeable barrier, which separate two phases and restrict transport of various chemical when a driving force is applied across the membrane (Baker, 2004), and also can described as a selective barrier between two phases, the term 'selective' being inherent to a membrane or a membrane process (Mulder, 1996). Membrane can be thick or thin, its structure can be homogenous or heterogeneous, solid or liquid, symmetric or asymmetric and transport can be active or passive, which passive transport can be cause by a pressure, concentration or a temperature difference (Mulder, 1996). This membrane process are increasingly used nowadays for environmental application such removal of carbon dioxide (CO_2).

2.2.2 Carbon dioxide (CO_2) removal

Carbon dioxide (CO_2) is one of the acid gases which have to be removed from natural gas, to prevent the corrosion problem and the global warming problems. The removal of the carbon dioxide (CO_2) is important as carbon dioxide (CO_2) can cause corrosion as well as greenhouse effect with approximately 55% of the global warming. Therefore, the removal of the carbon dioxide (CO_2) from the natural gas must be done before further bad impacts to environment and health. In industrial gas processing, there is an increasing interest in gas absorption processes for the selective removal of acid gases from the raw gas streams. The processes of removing carbon dioxide (CO_2) can be done by using membrane separation, chemical absorption, physical absorption, cryogenic methods, and biological fixation and by gas permeation (Mansourizadeh and Ismail, 2011b).

Absorption process can offer a very high selectivity and a high driving force for transport even at very low concentration in the reaction (Klaassen et al, 2008). Besides that, another advantages of absorption process over conventional contacting devices are have high surface area per unit contactor volume, independent control of gas and liquid flow rates without any flooding, loading, weeping, foaming or entrainment problems, small size, modular, and easy to scale up or down (Gabelman and Hwang, 1999).

Since 1980, much research has been completed to remove carbon dioxide (CO_2) from flue gas using gas-liquid membrane contactor system. For this purpose, researchers have considered a number of factors such as membrane materials, absorption solution, and membrane module to improve the performance of the removal of carbon dioxide (CO_2) (Rahbari Sisakht et al., 2012).

2.2.3 Advantages and disadvantages of membrane

Membranes process has numerous numbers of advantage and disadvantage compared to other conversional methods.

The advantages of membrane include:

- Membranes can be produced with extremely high selectivity for the components to be separated/remove. In general, the values of this selectivity are much higher than typical values for relative volatility for distillation operations.
- Because of the fact that a very large number of polymers and inorganic media can be used as membranes, there can be a great deal of control over separation/removal selectivity.
- Membrane processes are able to recover minor but valuable components from a main stream without substantial energy costs.
- Membrane processes are potentially better for the environment since the membrane approach require the use of relatively simple and non-harmful materials.

The disadvantages of membrane include:

- Membrane modules often cannot operate at much above room temperature. This is again related to the fact that most membranes are polymer-based, and that a large fraction of these polymers do not maintain their physical integrity at much above 100 ^oC. This temperature limitation means that membrane processes in a number of cases cannot be made compatible with chemical processes conditions very easily.
- Membrane processes can be saddled with major problems of fouling of the membranes while processing some type of feed streams. This fouling, especially if it is difficult to remove, can greatly restrict the permeation rate through the membranes and make them essentially unsuitable for such applications.

2.3 Membrane structure

The proper choice of membrane should be determined by their specific application. There are two type of membrane structure that commonly used which is asymmetric and isotropic membrane (nonporous and microporous). The different between these two structures are the physical and chemical properties (Nunes and Peinemann, 2006).

2.3.1 Symmetric and Asymmetric membranes

2.3.1.1 Symmetric membrane

Symmetrical membranes are the properties of the membrane do not change throughout the cross-section of the membrane. Typical thickness of symmetric membranes ranges roughly from 10-200 µm. The resistance to mass transfer is determined by the total membranes thickness. A decrease of membrane thickness results in an increased permeation rate.

2.3.1.2 Asymmetric membrane

Asymmetric or as known as anisotropic are non-uniform over the membrane cross section and they consist of a number of layers each with different structure permeability and chemical composition. The asymmetric consists of a very dense top layer with thickness about 0.1 to 0.5 µm supported by a porous sublayer about 50-150 µm. The asymmetric membranes combine high permeant flow, provided by a very thin selective top layer and reasonable stability (Mulder, 1996). Because the nature of this membrane itself have a thin top layer that acts as a selective barrier film, and a porous sublayer that offer good mechanical strange makes this membrane have been widely used for gas and liquid separation process.

2.3.2 Isotropic membrane

Isotropic membranes have a uniform composition structure all through, and they can be porous or dense. The resistance to mass transfer in these membranes are determined by the total membrane thickness. A decrease in membrane thickness brings about an increased permeation rate. Isotropic membrane divided by nonporous and microporous membrane.

2.3.2.1 Nonporous membrane

These types of membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. Dense membranes have the weakness of low flux unless they can be made extremely thin. Therefore, dense membrane properties are joined into the top "skin" layers of asymmetric membranes. The transmembrane of dense nonporous isotropic membrane fluxes through this membrane relatively make it too low for practical separation process and rarely used in membrane separation process. On the other hand, this nonporous isotropic membrane is commonly used in laboratory work to characterize the membrane properties. Most gas separation, pervaporation, and reverse osmosis processes use dense membrane to perform the separation (Baker, 2004).

2.3.2.2 Microporous membrane

This isotropic microporous membrane almost behave like fibre filter and separate by sieving mechanism that determined by the pore diameter and particle size. The pores in the membrane may vary between 1nm- 20 micron (Baker, 2004). By comparing with the isotropic nonporous membrane, the isotropic microporous membranes have higher fluxes and more widely used as microfiltration membrane. The microporous membrane acts as a fixed interface between the gas and the liquid phase without dispersing one phase into another that offers a flexible modular and energy efficient device (Mansourizadeh and Ismail, 2009). Besides, it is also used as inert spacers in a battery and fuel cell applications and as the rate controlling element in controlled drug delivery device (Hazah, 2012).

The simplest form of microporous membrane is a polymer film with cylindrical pores or capillaries. However, more commonly microporous membranes have a more open and random structure, with interconnected pores. They are very similar in structure and function to conventional filters. However, in contrast with conventional filters, these pores are extremely small, on the order of 0.01 to 10 micrometer in diameter (Baker, 2004).

2.3.2.3 Electrical Charged membrane

These types of membranes are also referred to as ion-exchange membranes. They can be dense or microporous, with the pore walls carrying fixed positively or negatively charged ions. A membrane fixed with positively-charged ions is called an anion-exchange membrane because it binds anions (negativeely charged ions) in the surrounding fluid. The reverse is true for a cation-exchange membrane.

Separation is accomplished mostly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is influenced by the charge and concentration of ions in the solution. This type of membranes is utilized for processing electrolyte solutions as a part of electro dialysis (Baker, 2004).

2.3.3 Liquid membrane

Liquid membranes have turn out to be progressively increased in the context of facilitated transport, which uses "carriers" to specifically transport components, for example, metal ions at a generally high rate over the membrane interface.

Generally, development of a thin fluid film is not an issue. Difficulty is encountered, however, in keeping up and controlling this film and its properties during a mass separation process. Reinforcement is important to avoid break-up of the film. Liquid membranes are utilized on a pilot-plant scale for selective removal of heavy-metal ions and organic solvents from industrial waste streams. They have also been utilized for the separation of oxygen and nitrogen.

2.4 Membrane module

A membrane module is a pack of the membrane area into the least volume, to lower the capital and operating cost with providing acceptable flow hydrodynamics in the vessel. The effectiveness of the membrane separation process usually depends on the module configuration because the active separation membrane area can affect the membrane module configuration. There are four type of membrane which is tubular, spiral wound, plate and frame and hollow fibres.

2.4.1 Tubular membrane module

The tubular module are now generally restricted to ultra-filtration, which is has advantage of resistance to membrane fouling outweighs the high cost. These modules enclose as many as 5 to 7 smaller tubes, each 0.5 to 1.0 cm in diameter (Hazah, 2012). The membrane is often on the inside of a tube and the feed solution is pumped through the tube and permeate is removed from each tube from each tube and sent to permeate collection header.

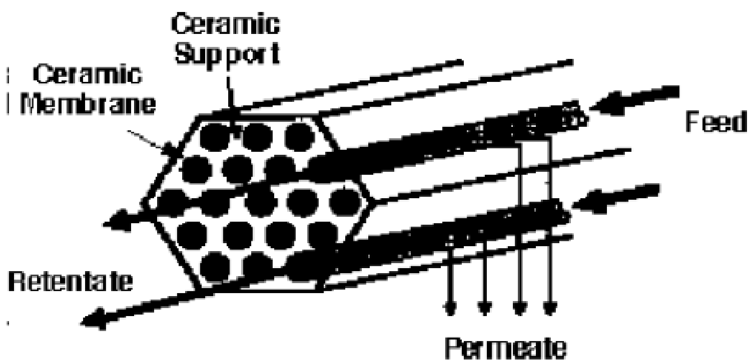

Figure 2-1: A schematic drawing of a tubular membrane module (Hazah, 2012).

2.4.2 Hollow fibe membrane module

The hollow fiber module also has been widely used for desalination that usually consists of bundle of hollow fibers in a pressure vessel. The system of hollow fiber module will pressurised from the shell side, and the filtrate passes along the fiber wall and exits through the open fiber ends. Bore-side of hollow fiber modules can also be used where the feed is circulated through the fiber (Mansourizadeh and Ismail, 2010a). The most advantages of hollow fiber modules are the ability to pack a very large membrane to single module.

Li and Chen (2005) reported that Qi and Cussler were the first to establish the idea of the hollow-fiber contactor using a microporous polypropylene (PP) hollow fiber membrane for absorption of carbon dioxide (CO_2) and aqueous sodium hydroxide (NaOH) solution was used as an absorbent. The fibers used in the contactor are generally not selective. Membranes with a higher selectivity have lower permeability and produce a smaller flux. Thus, the advantage of using non-selective membrane is potentially to get a higher flux.

For carbon dioxide (CO_2) absorption study, some of the microporous hydrophobic membrane was used, which are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). In this study, polyvinylidene fluoride (PVDF) is used because it is hydrophobic polymers dissolved in the same solvent, which can be used in phase-inversion process for the preparation of asymmetric membranes. Microporous PVDF membranes are also used in membrane contactors due to high hydrophobicity, high chemical resistance and reasonable cost of materials.

On the other hand, polyvinylidene fluoride (PVDF), another hydrophobic polymer, has good chemical and thermal resistance, and in contrast with aforementioned polymeric materials are soluble in common organic solvents. Hence it can easily be converted to asymmetric membranes via phase inversion method, resulting in easy controlled membrane structure and morphology (Rezaei et al, 2014).

Figure 2-2: A parallel flow hollow fiber module (Gabelman and Hwang, 1999)

2.4.3 Plate and frame membrane module

Plat and frame membrane module were one of the earliest type of membrane modules and were widely used in separation process. But, because of their relatively high cost they have replace in most application by spiral wound modules and also hollow fiber modules. Nowadays, the plate frame module used only in electrodialysis and pervaporation system in a limited number of reverse osmosis and ultrafiltration applications with highly fouling condition (Hazah, 2012).

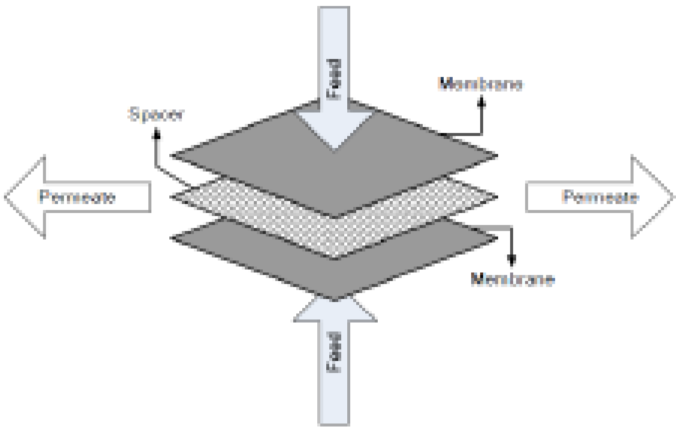

Figure 2-3: A schematic drawing of a plate and frame membrane module (Mulder, 1996)